JC17 Rec'd PCT/PTO 23 MAY 2001

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| FORM PTO-1390 (REV. 11-2000) U S DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE | ATTORNEY 'S DOCKET NUMBER 1-15397 |
| **TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371** | U S APPLICATION NO (If known, see 37 CFR 1.5 09/856584 |

| INTERNATIONAL APPLICATION NO. | INTERNATIONAL FILING DATE | PRIORITY DATE CLAIMED |
|---|---|---|
| PCT/GB99/03984 | 30 November 1999(30.11.99) | 1 December 1998 (01.12.98) |

TITLE OF INVENTION IMPROVEMENTS IN COATING GLASS

APPLICANT(S) FOR DO/EO/US JOSE MANUEL GALLEGO

Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. [X] This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. [ ] This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. [X] This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (21) indicated below.
4. [X] The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. [X] A copy of the International Application as filed (35 U.S.C. 371(c)(2))
   a. [X] is attached hereto (required only if not communicated by the International Bureau).
   b. [ ] has been communicated by the International Bureau.
   c. [ ] is not required, as the application was filed in the United States Receiving Office (RO/US).
6. [ ] An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
   a. [ ] is attached hereto.
   b. [ ] has been previously submitted under 35 U.S.C. 154(d)(4).
7. [ ] Amendments to the claims of the International Aplication under PCT Article 19 (35 U.S.C. 371(c)(3))
   a. [ ] are attached hereto (required only if not communicated by the International Bureau).
   b. [ ] have been communicated by the International Bureau.
   c. [ ] have not been made; however, the time limit for making such amendments has NOT expired.
   d. [ ] have not been made and will not be made.
8. [ ] An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371 (c)(3)).
9. [X] An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)).
10. [X] ~~An English language translation of the annexes to~~ A copy of the International Preliminary Examination Report ~~under PCT Article 36 (35 U.S.C. 371 (c)(5)~~).

**Items 11 to 20 below concern document(s) or information included:**

11. [ ] An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
12. [X] An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
13. [X] A FIRST preliminary amendment.
14. [ ] A SECOND or SUBSEQUENT preliminary amendment.
15. [ ] A substitute specification.
16. [ ] A change of power of attorney and/or address letter.
17. [ ] A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
18. [ ] A second copy of the published international application under 35 U.S.C. 154(d)(4).
19. [ ] A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
20. [X] Other items or information: One (1) sheet of formal drawings; return card; Express Mail Certificate; copy of cover page of published int'l appln.

JC18 Rec'd PCT/PTO 23 MAY 2001

| U.S. APPLICATION NO. (if known, see 37 CFR 1.5) 09/856584 | INTERNATIONAL APPLICATION NO PCT/GB99/03984 | ATTORNEY'S DOCKET NUMBER 1-15397 |
|---|---|---|

| | CALCULATIONS | PTO USE ONLY |
|---|---|---|
| 21. [X] The following fees are submitted:<br>**BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)):**<br>Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO ........... **$1000.00**<br>International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO ........ **$860.00**<br>International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO ........... **$710.00**<br>International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) ......... **$690.00**<br>International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) ............... **$100.00** | | |
| **ENTER APPROPRIATE BASIC FEE AMOUNT =** | $ 860.00 | |
| Surcharge of **$130.00** for furnishing the oath or declaration later than [ ] 20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492(e)). | $ – | |

| CLAIMS | NUMBER FILED | NUMBER EXTRA | RATE | $ | |
|---|---|---|---|---|---|
| Total claims | 36 - 20 = | 6 | x **$18.00** | $ 108.00 | |
| Independent claims | 3 - 3 = | 0 | x **$80.00** | $ – | |
| MULTIPLE DEPENDENT CLAIM(S) (if applicable) | | | + **$270.00** | $ – | |
| **TOTAL OF ABOVE CALCULATIONS =** | | | | $ 968.00 | |
| [ ] Applicant claims small entity status. See 37 CFR 1.27. The fees indicated above are reduced by 1/2. + | | | | $ – | |
| **SUBTOTAL =** | | | | $ 968.00 | |
| Processing fee of **$130.00** for furnishing the English translation later than [ ] 20 [ ] 30 months from the earliest claimed priority date (37 CFR 1.492(f)). | | | | $ – | |
| **TOTAL NATIONAL FEE =** | | | | $ 968.00 | |
| Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **$40.00** per property + | | | | $ 40.00 | |
| **TOTAL FEES ENCLOSED =** | | | | $ 1,008.00 | |
| | | | | **Amount to be refunded:** | $ |
| | | | | **charged:** | $ |

a. [XX] A check in the amount of $ 1,008.00 to cover the above fees is enclosed.

b. [ ] Please charge my Deposit Account No. ________ in the amount of $ ________ to cover the above fees. A duplicate copy of this sheet is enclosed.

c. [X] The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 13-1816 . ~~A duplicate copy of this sheet is enclosed.~~

d. [ ] Fees are to be charged to a credit card. **WARNING:** Information on this form may become public. **Credit card information should not be included on this form.** Provide credit card information and authorization on PTO-2038.

**NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137 (a) or (b)) must be filed and granted to restore the application to pending status.**

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"Express Mail" Label Number EL 469908459US

I hereby certify that this correspondence is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 on May 23, 2001 and is addressed to the Commissioner for Patents, Box PCT, Washington, D.C. 20231.

Kathleen J. Moore

(Signature of person mailing correspondence)

Kathleen J. Moore

(Typed name of person mailing correspondence)

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

| | |
|---|---|
| In re Application of: | ] |
| JOSE MANUEL GALLEGO | ] Group Art Unit: |
| | ] |
| Serial No. | ] |
| Filed: | ] Examiner: |
| | ] |
| Filing Under 35 U.S.C. 371 in | ] |
| the DO/EO/US off PCT/GB99/03984 | ] |
| filed 30 November 1999 | ] |
| | ] |
| For:IMPROVEMENTS IN COATING GLASS | ] Attorney Docket 1-15397 |

May 21, 2001

Commissioner for Patents
Box PCT
Washington, D.C. 20231

PRELIMINARY AMENDMENT

Honorable Sir:

Prior to the first Office Action and before examining the claims, please amend the application being filed concurrently herewith under 35 U.S.C. 371 as follows:

IN THE CLAIMS

Please amend claims 3-8, 10, 12-13, 16-17, 19-20, 24-26 and 28-31 as follows.

3. (Amended) A process according to claim 1 wherein the underlayer comprises a silicon oxide.

4. (Amended) A process according to claim 1 wherein the underlayer comprises a silicon oxide containing carbon.

5. (Amended) A process according to claim 1 wherein the pyrolytic deposition of the underlayer comprises contacting the glass substrate with a fluid mixture containing a silicon source, an oxygen source and a carbon source under conditions such that a silicon oxide layer, preferably containing carbon, is deposited.

6. (Amended) A process according to claim 5 wherein the fluid mixture is a vapor mixture.

7. (Amended) A process according to claim 1 wherein the underlayer comprises silicon oxide containing nitrogen.

8. (Amended) A process according to claim 1 wherein the underlayer is deposited on the glass substrate when the glass substrate is at a temperature in the range 450°C to 800°C.

10. (Amended) A process according to claim 1 wherein the underlayer is deposited on to a glass ribbon during the float glass production process at substantially atmospheric pressure.

12. (Amended) A process according to claim 1 wherein the reflective metal layer comprises silver or aluminium.

13. (Amended) A process according to claim 1 wherein an anti-reflection layer is deposited by a vacuum deposition process on to the coated glass after deposition of the reflective metal layer.

16. (Amended) A process according to claim 13 wherein a second reflective metal layer and a second anti-reflection layer are sequentially deposited by a vacuum deposition process after deposition of the first anti-reflection layer.

17. (Amended) A process according to claim 1 additionally comprising a heat treatment step wherein the heat-treatable low emissivity coated glass is subjected to a temperature in the range 400 to 750°C in an oxidising atmosphere.

19. (Amended) A process according to claim 17 wherein the visible transmission of the coated glass is increased by the heat-treatment step.

20. (Amended) A coated glass produced by a process according to claim 1.

24. (Amended) A coated glass according to claim 21 wherein the underlayer has a refractive index in the range 1.5 to 3.

25. (Amended) A coated glass according to claim 21 wherein the underlayer has a thickness in the range 30 to 100 nm.

26. (Amended) A coated glass according to claim 21 wherein the reflective metal layer has a thickness in the range 5 to 30 nm.

28. (Amended) A coated glass according to claim 21 wherein the anti-reflection layer has a thickness in the range 30 nm to 90 nm.

29. (Amended) A coated glass according to claim 21 wherein the coated glass has a normal emissivity of below 0.2.

30. (Amended) A coated glass according to claim 21 wherein the coated glass has a normal emissivity of below 0.1.

31. (Amended) A coated glass according to claim 21 wherein the coated glass has been heat treated by heating it to a temperature in the range 400 to 700°C in an oxidising atmosphere.

Please delete claim 37.

## REMARKS

Applicant has amended the application to eliminate multiple dependencies and to adapt the claims to U.S. patent practice. A separate marked up copy of the amended claims is attached hereto entitled "Version With Markings To Show Changes Made".

Claims 3-8, 10, 12-13, 16-17, 19-20, 24-26, and 28-31 have been amended and claim 37 has been deleted. Claims 1-36 are currently pending in the present application. No new matter has been added by any of these amendments.

Favorable consideration of the application as amended is respectfully requested.

Respectfully submitted,

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**Version With Markings To Show Changes Made**

3. (Amended) A process according to [either] claim 1 [or claim 2] wherein the underlayer comprises a silicon oxide.

4. (Amended) A process according to [any one of claims 1-3] claim 1 wherein the underlayer comprises a silicon oxide containing carbon.

5. (Amended) A process according to [any one of claims 1-4] claim 1 wherein the pyrolytic deposition of the underlayer comprises contacting the glass substrate with a fluid mixture containing a silicon source, an oxygen source and a carbon source under conditions such that a silicon oxide layer, preferably containing carbon, is deposited.

6. (Amended) A process according to claim 5 wherein the fluid mixture is a [vapour] vapor mixture.

7. (Amended) A process according to [any one of claims 1-3] claim 1 wherein the underlayer comprises silicon oxide containing nitrogen.

8. (Amended) A process according to [any one of the preceding claims] claim 1 wherein the underlayer is deposited on the glass substrate when the glass substrate is at a temperature in the range 450°C to 800°C.

10. (Amended) A process according to [any one of preceding claims] claim 1 wherein the underlayer is deposited on to a glass ribbon during the float glass production process at substantially atmospheric pressure.

12. (Amended) A process according to [any one of the preceding claims] claim 1 wherein the reflective metal layer comprises silver or aluminium.

13. (Amended) A process according to [any one of the preceding claims] claim 1 wherein an anti-reflection layer is deposited by a vacuum deposition process on to the coated glass after deposition of the reflective metal layer.

16. (Amended) A process according to [any one of claims 13-15] claim 13 wherein a second reflective metal layer and a second anti-reflection layer are sequentially deposited by a vacuum deposition process after deposition of the first anti-reflection layer.

17. (Amended) A process according to [any one of the preceding claims] claim 1 additionally comprising a heat treatment step wherein the heat-treatable low emissivity coated glass is subjected to a temperature in the range 400 to 750°C in an oxidising atmosphere.

19. (Amended) A process according to [either] claim 17 [or claim 18] wherein the visible transmission of the coated glass is increased by the heat-treatment step.

20. (Amended) A coated glass produced by a process according to [any one of the preceding claims] claim 1.

24. (Amended) A coated glass according to [any one of claims 21-23] claim 21 wherein the underlayer has a refractive index in the range 1.5 to 3.

25. (Amended) A coated glass according to [any one of claims 21-24] claim 21 wherein the underlayer has a thickness in the range 30 to 100 nm.

26. (Amended) A coated glass according to [any one of claims 21-25] claim 21 wherein the reflective metal layer has a thickness in the range 5 to 30 nm.

28. (Amended) A coated glass according to [any one of claims 21-27] claim 21 wherein the anti-reflection layer has a thickness in the range 30 nm to 90 nm.

29. (Amended) A coated glass according to [any one of claims 21-28] claim 21 wherein the coated glass has a normal emissivity of below 0.2.

30. (Amended) A coated glass according to [any one of claims 21-29] claim 21 wherein the coated glass has a normal emissivity of below 0.1.

31. (Amended) A coated glass according to any one of claims 21-30] claim 21 wherein the coated glass has been heat treated by heating it to a temperature in the range 400 to 700°C in an oxidising atmosphere.

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JC18 Rec'd PCT/PTO 23 MAY 2001



Improvements in Coating Glass.

This invention relates to a process for the production of a heat-treatable low emissivity coated glass and to a heat-treatable low emissivity coated glass.

It is known that transparent glass substrates with a thin reflective metal coating, typically silver 5 nm to 30 nm thick, may be produced with low emissivity and a high visible light transmission i.e. which reflect a high proportion of infra-red radiation incident upon them but allow visible radiation to pass through. The use of such coatings on window glass leads to a reduction in heat loss. For optimum light transmission, the silver layers are sandwiched between thin anti-reflection layers of metal oxide. Such low emissivity coatings are produced by vacuum deposition processes, especially sputtering, and normally comprise a thin layer of silver sandwiched between two layers of metal oxide. Such coatings are described, for example, in UK patent specification GB 2 129 831.

Unfortunately, such low emissivity coatings are not stable to heating in air, and the coating loses its properties of low emissivity and high light transmission when the coated glass is subjected to a thermal cycle which cycle is required for bending or toughening the glass. To obtain a toughened or bent glass substrate bearing a low emissivity reflective metal coating that has high light transmission it has been necessary to either bend and/or toughen the glass before depositing the reflective metal coating or to deposit an additional, protective layer over the reflective metal layer before bending/toughening. GB patent 2 186 001B describes this problem and a process for the production of a bent and/or

toughened silver coated glass substrate wherein an additional metal layer of aluminium, titanium, zinc or tantalum is deposited over the silver layer. The additional metal layer protects the silver layer beneath it from degradation during the bending or toughening thermal cycle by acting as a barrier layer between the silver layer and the oxidising atmosphere.

The applicants have now discovered that the above problem may be alleviated by depositing an underlayer onto glass substrate using a pyrolytic deposition process and subsequently depositing a reflective metal layer onto the coated substrate.

According to one aspect of the present invention there is provided a process for the production of a heat-treatable low emissivity coated glass that comprises the steps of

a) depositing an underlayer onto a glass substrate, and

b) subsequently depositing a reflective metal layer by a vacuum deposition method, characterised in that the underlayer is deposited by a pyrolytic deposition process.

Surprisingly, the underlayer deposited by a pyrolytic deposition process provides protection to the reflective metal layer on heat-treatment despite its position underneath the reflective metal layer. In preferred embodiments of the invention a barrier layer is unnecessary which is advantageous because then fewer layers need be deposited reducing the time needed for the process and so increasing production rates.

Normal emissivity is defined in International Standard ISO 12092:1994 (F), Annex A as $\varepsilon_N = 1 - R_N$ where $R_N$ is the normal reflectance over the wavelength range 5.5 μm to 50 μm at 283 K. Low emissivity coatings as discussed herein

are those which have a normal emissivity of below about 0.4. The lower the emissivity of the coated glass the better are the heat rejecting properties of the glass.

Usually, the reflective metal layer is deposited directly on the underlayer, but one or more intermediate layers (e.g. of metal oxide) may be deposited between the underlayer and the reflective metal layer if, for example it is desired to deposit an anti-reflection layer or anti-reflection layers additional to the underlayer. Layers may also be deposited beneath the underlayer.

Pyrolytic deposition processes are processes which are usually carried out at substantially atmospheric pressure wherein a fluid is directed onto a hot substrate under conditions such that a coating is formed on the substrate. Processes wherein the fluid is a liquid are termed spray deposition processes and processes wherein the fluid is a vapour are termed chemical vapour deposition (CVD) processes. The preferred pyrolytic deposition process for deposition of the underlayer is CVD because it may be performed on line (i.e. during the float glass production process) and produces good quality coating layers.

It is thought that any pyrolytically deposited material could be advantageously used as an underlayer in the present invention. For example, the underlayer may comprise silicon oxide, silicon oxide containing carbon (often referred to as silicon oxycarbide and which may be deposited as described in European patent application 275 662 A), silicon oxide containing nitrogen (often referred to as silicon oxynitride and which may be deposited as described in GB patent 2 031 756 B), titanium oxide, tin oxide, titanium nitride, silicon nitride, silicon carbide, silicon or a mixture comprising one or more of these materials. The preferred underlayer comprises a silicon

oxide, especially a silicon oxide containing carbon, because silicon oxide layers are relatively easily deposited by CVD in a range of stoichiometries (and hence a range of refractive indices).

If silicon oxide is selected as the underlayer material, pyrolytically depositing the underlayer preferably comprises contacting the glass substrate with a fluid mixture containing a silicon source, an oxygen source and a carbon source under conditions such that a silicon oxide layer, preferably containing carbon, is deposited. Preferably, the fluid mixture is a vapour mixture.

The underlayer will usually be deposited on the glass substrate when the glass substrate is at a temperature in the range 450°C to 800°C, especially when the glass substrate is at a temperature in the range 600°C to 780°C.

Preferably, the underlayer is deposited on to a glass ribbon during the float glass production process at substantially atmospheric pressure in which case the glass ribbon will usually be cut into sheets after deposition of the underlayer (and before deposition of other layers including the reflective metal and any subsequent layers) for storage or convenient transport from the float glass production facility to the vacuum deposition facility.

The reflective metal layer may comprise silver or aluminium, preferably silver.

A vacuum deposition process is one which is usually performed at a pressure of lower than about 0.1 mbar and includes such methods as sputtering, reactive sputtering, evaporation and other forms of physical vapour deposition. The preferred vacuum deposition method for depositing a reflective metal layer is sputtering.

Usually, an anti-reflection layer is deposited by a vacuum deposition process on to the coated glass after deposition of the reflective metal layer. Preferably, the anti-reflection layer comprises a metal oxide, more preferably the anti-reflection layer comprises zinc oxide or tin oxide. More than one anti-reflection layer may be deposited.

If an anti-reflection layer is deposited by reactive sputtering in an oxidising atmosphere comprising, for example, more than 70% by volume oxygen, a further protective layer is preferably deposited on the reflective metal layer before the sputtering step so as to protect the reflective metal layer from degradation by the oxidising atmosphere. The further protective layer preferably comprises inconel or nichrome. Other layers may also be deposited between the reflective metal layer and anti-reflection layer(s).

The invention also provides a process for the production of coated glass having a coating with more than one reflective metal layer. Thus, in an embodiment of the invention a second reflective metal layer and a second anti-reflection layer are sequentially deposited by a vacuum deposition process after deposition of the first anti-reflection layer. In this embodiment of the invention (where the coated glass has two reflective metal layers) the glass will usually have lower emissivity than in the single reflective metal layer embodiment and also, with appropriate layer thicknesses, a reduced transmission of solar heat.

The process may additionally comprise a heat treatment step wherein the heat-treatable low emissivity coated glass is subjected to a temperature in the range 400°C to 750°C in an oxidising atmosphere, which is usually

directed to the production of bent and/or toughened coated glass. Surprisingly and advantageously, the visible transmission of the heat-treatable low emissivity coated glass may be increased by the heat-treatment step.

In a further aspect, the invention provides a heat-treatable low emissivity coated glass comprising a glass substrate having a multilayer coating on a surface, said multilayer coating comprising a pyrolytically deposited underlayer, a vacuum deposited reflective metal layer and a vacuum deposited anti-reflection layer.

Preferably the underlayer comprises a silicon oxide, more preferable a silicon oxide containing carbon and advantageously, the underlayer will have a refractive index in the range 1.5 to 3 because an underlayer with a refractive index in this range enables a coating with a low visible light reflection to be produced (i.e. this range of refractive index is suitable for an anti-reflection underlayer). In most embodiments of the invention the underlayer has a thickness in the range 30 to 100 nm.

The reflective metal layer usually comprises silver or aluminium and preferably has a thickness in the range 5 to 30 nm, more preferably in the range 7 to 18 nm. At thicknesses lower than 7 nm the reflective metal layer may be discontinuous (this results from the growth mechanism of a layer and may occur even on a flat substrate) and will then not possess the properties of the bulk metal (resulting in poor infra red reflecting properties), whereas thicknesses higher than 18 nm may cause the coated glass to have too high a reflectivity to visible light.

The anti-reflection layer beneficially has a thickness in the range 30 nm to 90 nm.

Coated glass according to the invention will usually have a normal emissivity of below 0.2, preferably below 0.1. Coated glass according to the invention which has been heat treated by heating it to a temperature in the range 400 to 700°C in an oxidising atmosphere will usually have a normal emissivity of below 0.2, preferably below 0.1, after the heat treatment step. Surprisingly and advantageously, heat treatment tends to reduce the emissivity of those embodiments of the invention having a single reflective metal layer.

It is thought that a pyrolytically deposited underlayer reduces oxygen induced degradation during heat treatment in an oxidising atmosphere by scavenging oxygen that would otherwise attack the silver layer. Underlayers that scavenge oxygen deposited using methods other than pyrolysis may also be useful as underlayers in the invention.

Thus, in a further aspect of the present invention a heat-treatable low emissivity coated glass comprises a glass substrate having a multilayer coating on one surface, said multilayer coating comprising an oxygen scavenging underlayer, a vacuum deposited reflective metal layer and a vacuum deposited anti-reflection layer.

The oxygen scavenging underlayer may comprise a material deficient in oxygen that has the potential to bind oxygen in preference to the reflective metal layer (usually a silver layer). An example of a material likely to be suitable as an oxygen scavenging underlayer is oxygen deficient silicon oxide ($SiO_x$ where x is less than 2).

Coated glasses produced by the process of the present invention have uses in many areas of glass use including as a glazing pane in a multiple glazing unit or as a

glazing pane in a laminated glass which will also comprise a polymer interlayer (usually of polyvinylbutyral) and a second glazing pane.

So that the invention may be better understood reference will now be made to the following drawings in which:-

Figure 1 illustrates schematically a section through a coated glass having a single reflective metal layer, the coated glass produced by a process according to the invention.

Figure 2 illustrates schematically a section through a coated glass having two reflective metal layers, the coated glass produced by a process according to the invention.

Referring to Fig. 1, a low emissivity coated glass 2 with a single silver layer 8 comprises a glass substrate 4, a pyrolytically deposited underlayer 6 of silicon oxide containing carbon of thickness 58 nm, a DC magnetron vacuum sputtered silver layer 8 of thickness 12 nm and a further layer of sputtered zinc oxide 10 of thickness 38 nm. The underlayer 6 is deposited by on line chemical vapour deposition. The underlayer 6 and the zinc oxide layer 10 act as anti-reflection layers.

Referring to Fig. 2, a low emissivity coated glass 12 with two silver layers 18 and 22 comprises a glass substrate 14, a pyrolytically deposited underlayer 16 of silicon oxide containing carbon of thickness 58 nm, and DC magnetron vacuum sputtered layers of: silver 18 of thickness 8.1 nm, zinc oxide 20 of thickness 85 nm, silver 22 of thickness 8.4 nm, and zinc oxide 24 of thickness 49 nm. A two silver layer low emissivity coating can provide greater infra red reflection compared to a single silver layer low emissivity coating and can also provide good

solar control properties (i.e. reducing transmitted solar heat).

The invention is further illustrated by the following Examples, in which vacuum deposited coatings were applied to glass substrates coated with an underlayer of silicon oxide containing carbon.

The silicon oxycarbide (silicon oxide containing carbon) underlayer was deposited substantially as described in European patent application EP 0 275 662A by applying a flowing gaseous mixture to the upper surface of a glass ribbon during the float glass production process using a water-cooled graphite coater. The gaseous mixture was applied at a position where the glass temperature was approximately 773°C as the ribbon advanced at a ribbon speed of 127 m/hr over the float bath. The gaseous mixture comprised nitrogen (as carrier gas, flow rate 0.92 kg/hr), monosilane ($SiH_4$, flow rate 0.06 kg/hr), ethylene (flow rate 1.84 kg/hr) and carbon dioxide (flow rate 2.31 kg/hr). The gaseous mixture was caused to flow parallel to the glass surface in the direction of movement of the glass under laminar flow conditions using an apparatus as described in GB patent specification 1 507 966 extending over the 2 m width of the glass ribbon, and with a path of travel extending approximately 0.1 m down-ribbon. The thickness of the glass was about 2.8 mm.

At the end of the float line, samples of the glass coated with the underlayer were cut from the glass ribbon. Coating layers were vacuum deposited on the samples at room temperature by sputtering or reactive sputtering using an Airco Temescal ILS 1600 sputtering plant and DC magnetron sputtering using metal targets of 99.9% purity or better. Deposition conditions for layers comprising

silver, inconel, tin (IV) oxide and zinc oxide are described in Table 1.

The layer materials and layer thicknesses for the underlayer and the vacuum deposited coatings in the Examples are described in Table 2.

Table 3 describes the optical properties of the coated glasses of the Examples before and after (the values after heat treatment are in brackets) heat treatment to simulate toughening. The heat treatment consisted of subjecting the coated glass to a temperature of 640°C in air for 1.5 minutes. The visible transmission, reflection and the transmission and reflection colours in Table 3 were measured using an Hitachi U400 spectrophotometer and/or a Perkin Elmer 883 spectrophotometer, and calculated using the methods described in International Standard ISO 12092:1994 (F) and other standard methods. The thicknesses of the layers were determined by computer fitting the spectra and by profilometry (Sloan Dektak II profilometer) after appropriate etching treatment (e.g. with aqueous hydrofluoric acid).

Table 1

| | Layer Material | | | |
|---|---|---|---|---|
| | Silver | Inconel | Tin Oxide | Zinc Oxide |
| Power Density ($W/cm^2$) | 0.61 | 0.36 | 3.6 | 3.8 |
| Gas Pressure ($10^{-3}$ mbar) | 9.3 | 11.8 | 6.7 | 6.8 |
| Gas Composition (%) Ar | 100 | 100 | 0 | 30 |
| $O_2$ | 0 | 0 | 100 | 70 |
| Target - Substrate Distance (cm) | 11 | 11 | 11 | 11 |
| Substrate speed (cm/s) | 2.7 | 2.9 | 3.1 | 3.1 |
| Number of passes to obtain: | 8 | 8 | 10 | 10 |
| Thickness (Å) | 102 | 10 | 362 | 340 |

Table 2

| Layers | Example 1 | Example 2 | Example 3 | Example 4 |
|---|---|---|---|---|
| Silicon Oxide underlayer (nm) | 58 | 58 | 58 | 58 |
| First Silver Layer (nm) | 11.9 | 8.1 | 11.4 | 7.9 |
| First Inconel Layer (nm) | - | - | 0.65 | 0.56 |
| First Dielectric Layer (nm) | 38 (ZnO) | 85 (ZnO) | 42 ($SnO_2$) | 83 ($SnO_2$) |
| Second Silver Layer (nm) | - | 8.4 | - | 8.8 |
| Second Inconel Layer (nm) | - | - | - | 0.54 |
| Second Dielectric Layer (nm) | - | 49 (ZnO) | - | 48 ($SnO_2$) |

Table 3

| | Example 1 | Example 2 | Example 3 | Example 4 |
|---|---|---|---|---|
| | Value before (after) heat treatment | Value before (after) heat treatment | Value before (after) heat treatment | Value before heat treatment |
| Visible Transmission % | 76.3 (78.2) | 74.1 (74.9) | 74.5 (78.1) | 73.2 |
| Visible Reflection % | 9.5 (9.1) | 5.4 (5.2) | 10.7 (9.2) | 6.4 |
| Transmission Colour | | | | |
| a* | -4.2 (-3.9) | -3.9 (-4.2) | -5.1 (-3.4) | -4.6 |
| b* | 5.3 (4.9) | 5.1 (5.4) | 7.2 (7.4) | 6.7 |
| L | 91 (92) | 88 (88) | 89 (91) | 86.2 |
| Reflection Colour | | | | |
| a* | 8.2 (7.9) | 3.1 (3.5) | 10.4 (8.9) | 3.4 |
| b* | -3.2 (-3.8) | 2.5 (3.2) | -5.3 (-4.8) | 5.5 |
| L | 35.2 (33.5) | 31.2 (29.5) | 38.7 (34.5) | 30.2 |
| Normal Emissivity | 0.072 (0.069) | 0.060 (0.065) | 0.076 (0.072) | 0.066 |

Claims

1. A process for the production of a heat-treatable low emissivity coated glass that comprises the steps of
   a) depositing an underlayer onto a glass substrate and
   b) subsequently depositing a reflective metal layer by a vacuum deposition method, characterised in that the underlayer is deposited by a pyrolytic deposition process.

2. A process according to claim 1 wherein the reflective metal layer is deposited directly on the underlayer.

3. A process according to either claim 1 or claim 2 wherein the underlayer comprises a silicon oxide.

4. A process according to any one of claims 1-3 wherein the underlayer comprises a silicon oxide containing carbon.

5. A process according to any one of claims 1-4 wherein the pyrolytic deposition of the underlayer comprises contacting the glass substrate with a fluid mixture containing a silicon source, an oxygen source and a carbon source under conditions such that a silicon oxide layer, preferably containing carbon, is deposited.

6. A process according to claim 5 wherein the fluid mixture is a vapour mixture.

7. A process according to any one of claims 1-3 wherein the underlayer comprises silicon oxide containing nitrogen.

8. A process according to any one of the preceding claims wherein the underlayer is deposited on the glass substrate when the glass substrate is at a temperature in the range 450°C to 800°C.

9. A process according to claim 8 wherein the underlayer is deposited on the glass substrate when the glass substrate is at a temperature in the range 600°C to 780°C.

10. A process according to any one of preceding claims wherein the underlayer is deposited on to a glass ribbon during the float glass production process at substantially atmospheric pressure.

11. A process according to claim 10 wherein the glass ribbon is cut into sheets after deposition of the underlayer.

12. A process according to any one of the preceding claims wherein the reflective metal layer comprises silver or aluminium.

13. A process according to any one of the preceding claims wherein an anti-reflection layer is deposited by a vacuum deposition process on to the coated glass after deposition of the reflective metal layer.

14. A process according to claim 13 wherein the anti-reflection layer comprises a metal oxide.

15. A process according to claim 14 wherein the anti-reflection layer comprises zinc oxide or tin oxide.

16. A process according to any one of claims 13-15 wherein a second reflective metal layer and a second anti-reflection layer are sequentially deposited by a vacuum deposition process after deposition of the first anti-reflection layer.

17. A process according to any one of the preceding claims additionally comprising a heat treatment step wherein the heat-treatable low emissivity coated glass is subjected to a temperature in the range 400 to 750°C in an oxidising atmosphere.

18. A process according to claim 17 wherein the heat treatment step is directed to the production of bent and/or toughened coated glass.

19. A process according to either claim 17 or claim 18 wherein the visible transmission of the coated glass is increased by the heat-treatment step.

20. A coated glass produced by a process according to any one of the preceding claims.

21. A heat-treatable low emissivity coated glass comprising a glass substrate having a multilayer coating on one surface, said multilayer coating comprising a pyrolytically deposited underlayer, a vacuum deposited reflective metal layer and a vacuum deposited anti-reflection layer.

22. A coated glass according to claim 21 wherein the underlayer comprises a silicon oxide.

23. A coated glass according to claim 22 wherein the underlayer comprises a silicon oxide containing carbon.

24. A coated glass according to any one of claims 21-23 wherein the underlayer has a refractive index in the range 1.5 to 3.

25. A coated glass according to any one of claims 21-24 wherein the underlayer has a thickness in the range 30 to 100 nm.

26. A coated glass according to any one of claims 21-25 wherein the reflective metal layer has a thickness in the range 5 to 30 nm.

27. A coated glass according to claim 26 wherein the reflective metal layer has a thickness in the range 7 to 18 nm.

28. A coated glass according to any one of claims 21-27 wherein the anti-reflection layer has a thickness in the range 30 nm to 90 nm.

29. A coated glass according to any one of claims 21-28 wherein the coated glass has a normal emissivity of below 0.2.

30. A coated glass according to any one of claims 21-29 wherein the coated glass has a normal emissivity of below 0.1.

31. A coated glass according to any one of claims 21-30 wherein the coated glass has been heat treated by heating it to a temperature in the range 400 to 700°C in an oxidising atmosphere.

32. A coated glass according to claim 31 wherein the coated glass has a normal emissivity of below 0.2 after the heat treatment step.

33. A coated glass according to claim 32 wherein the coated glass has a normal emissivity of below 0.1 after the heat treatment step.

34. A heat-treatable low emissivity coated glass comprising a glass substrate having a multilayer coating on one surface, said multilayer coating comprising an oxygen scavenging underlayer, a vacuum deposited reflective metal layer and a vacuum deposited anti-reflection layer.

35. A multiple glazing unit comprising a first glazing pane of a coated glass according to claim 34 and a second glazing pane.

36. Laminated glass comprising a first glazing pane of a coated glass according to claim 34, an interlayer and a second glazing pane.

37. A process for producing coated glass substantially as herein described with particular reference to the Examples 1-4.

## Abstract

## Improvements in Coating Glass

A process for the production of a heat-treatable low emissivity coated glass that comprises the steps of depositing an underlayer onto a glass substrate and subsequently depositing a reflective metal layer by a vacuum deposition process, wherein the underlayer is deposited by a pyrolytic deposition process. Preferably an anti-reflection layer is deposited by a vacuum deposition process on to the coated glass after deposition of the reflective metal layer. The underlayer may comprise a silicon oxide, the reflective metal layer may comprise silver and the anti-reflection layer may comprise a metal oxide, especially tin oxide or zinc oxide. The coated glass preferably has an emissivity of below 0.2 after heat treatment in an oxidising atmosphere.

Figure 1

Fig.1.

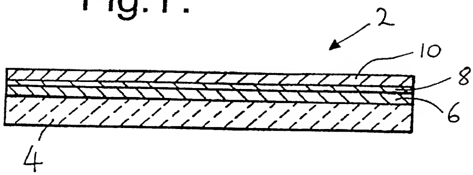
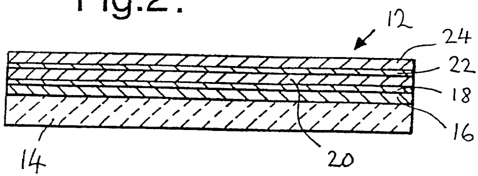



Fig.2.



**COMBINED DECLARATION AND POWER OF ATTORNEY IN ORIGINAL APPLICATION**

ATTORNEY DOCKET NO. 1-15397

As a below named inventor, I hereby declare that:

My residence, post office address, and citizenship are as stated below next to my name,

I believe that I am the original, first, and sole inventor (if only one name is listed below) or an original, first, and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

IMPROVEMENTS IN COATING GLASS

the specification of which

(check one) XX is attached hereto, as a filing under 35 USC 371.

____ was filed on ________
as U.S. Serial No. ________
and was amended on ________.

X was filed on 30 November 1999
as PCT Int'l Application No. PCT/GB99/03984
and was amended on ________.

I hereby state that I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information, which is material to patentability as defined in 37, Code of Federal Regulations, § 1.56,

X and which is material to the examination of this application, namely, information where there is a substantial likelihood that a reasonable Examiner would consider it important in deciding whether to allow the application to issue as a patent; and

____ if this is a continuation-in-part application, information that occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application, in accordance with 37 CFR 1.63(e); and

____ in compliance with this duty, there is attached an information disclosure statement, in accordance with 37 CFR 1.98.

I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed:

Prior Foreign Application(s)

| | | | Priority Claimed | |
|---|---|---|---|---|
| 9826293.4 | UNITED KINGDOM | 01 December 1998 | XX | |
| (Number) | (Country) | (Day/Month/Year Filed) | Yes | No |
| | | | | |
| (Number) | (Country) | (Day/Month/Year Filed) | Yes | No |

I hereby claim the benefit under Title 35, United States Code, §120 of any United States application(s) listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application in the manner provided by the first paragraph of Title 35, United States Code, §112, I acknowledge the duty to disclose material information as defined in Title 37, Code of Federal Regulations, §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

| | | |
|---|---|---|
| | | |
| (Appln. Serial No.) | (Filing Date) | (Status)<br>(patented, pending, abandoned) |
| | | |
| (Appln. Serial No.) | (Filing Date) | (Status)<br>(patented, pending, abandoned) |

I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith with full power of substitution and revocation: Phillip S. Oberlin, Reg. No. 19,066; D. Edward Dolgorukov, Reg. No. 26,266; Donald A. Schurr, Reg. No. 34,247; Mark A. Hixon, Reg. No. 44,766; Stephen P. Evans, Reg. No. 47,281; and Angelica M. Colwell, Reg. No. 46,637. Address all telephone calls to Donald A. Schurr at telephone number (419) 249-7145. Address all correspondence to MARSHALL & MELHORN, LLC, Four Seagate - 8th Floor, Toledo, Ohio 43604, Attention: Donald A. Schurr.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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Full name of fourth joint inventor, if any ____________

Fourth Inventor's signature ____________ Date ______

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Citizenship ______ Post Office Address ____________